which ν(CO) bands are observed at 1970 and 1955 cm^{-1}.

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Dinuclear Uranium Alkoxides. Preparation and Structures of $KU_2(OCMe_3)_9$, $U_2(OCMe_3)_9$, and $U_2(OCHMe_2)_{10}$, Containing [U(IV),U(IV)], [U(IV),U(V)], and [U(V),U(V)], Respectively

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The structural results by X-ray crystallography are reported for three uranium alkoxides, two of which are new compounds. All three are dinuclear in the solid state, and they contain the following combinations of oxidation states: [U(IV),U(IV)], [U(V),U(IV)] and [U(V),U(V)]. $K[U_2(OCMe_3)_9]\cdot C_6H_{14}$: monoclinic, $P2_1/c$, a = 10.713 (3) Å, b = 25.990 (8) Å, c = 19.480 (6) Å, β = 91.13 (5)°, Z = 4. $U_2(OCMe_3)_9$: orthorhombic, $Pbcm$, a = 13.749 (7) Å, b = 19.977 (7) Å, c = 16.923 (8) Å, Z = 4. $U_2(OCHMe_2)_{10}$: triclinic, $P\bar{1}$, a = 10.974 (3) Å, b = 12.226 (3) Å, c = 10.002 (2) Å, α = 111.56 (2)°, β = 110.09 (2)°, γ = 67.87 (2)°, Z = 1. The first two contain confacial bioctahedra with U···U distances of 3.631 (2) and 3.549 (1) Å, respectively. The $U_2(OCHMe_2)_{10}$ molecule consists of edge-sharing octahedra with a U···U distance of 3.789 (1) Å. The terminal alkoxide groups in all three compounds display nearly linear U–O–C arrangements, with U–O–C bond angles between 160 and 176°. This appears to be a general feature of uranium alkoxides and suggests a high degree of O $\pi \rightarrow$ U contribution to the metal–oxygen bonds.

Introduction

It is now well established that the group 6 transition elements chromium, molybdenum, and tungsten, and especially the last two, have a pronounced tendency to form metal–metal bonds.[1] In particular, molybdenum and tungsten in their oxidation states III–V regularly exhibit bonds of orders 3, 2, or 1 in the presence of alkoxide ligands. We therefore reasoned that if uranium, formally a group 6 element, were to have any tendency to resemble molybdenum and tungsten in forming metal–metal bonds, this tendency might well manifest itself in the structures of uranium alkoxides. We recognized, of course, that for uranium the nature of the valence shell is somewhat different because of the participation of the 5f orbitals. It is known that the radial extent of these wave functions brings them significantly into or beyond the same spacial region as the 6s and 7p shell[2] and there is evidence from photoelectron spectroscopy and electronic absorption spectra that 5f orbitals participate in some forms of bonding to the actinide elements.[3]

By following the procedure of Gilman[4] for the preparation of $[U(OCMe_3)_4]_n$, we obtained a previously unreported type of U^{IV} compound, $K[U_2(O_2CMe_3)_9]$ (**1**). Though it is formally an ionic compound, **1** is soluble in hexane where, at 5 °C, it is slowly and spontaneously transformed into the U^{IV}/U^{V} compound $U_2(O_2CMe_3)_9$ (**2**). We have also obtained the previously known U^{V}/U^{V} compound $U_2(OCHMe_2)_{10}$ (**3**). The crystal and molecular structures of all three of these compounds have been determined and are reported here.

Experimental Section

Standard high-vacuum, Schlenk, and inert-atmosphere glovebox procedures were used throughout this study. Solvents were dried over Na/K alloy and distilled under argon. The alcohols were dried over activated molecular sieves and degassed by pump–freeze procedures. Commercial UCl_4, purified by the procedure of Marks,[5] was used.

Preparation of the Compounds. $U_2(O\text{-}i\text{-}Pr)_{10}$ (**3**) was prepared by alcohol exchange from $[U(OC_2H_5)_5]_n$ following published procedures.[6] Single crystals of suitable size were grown by slow sublimation as well as by slowly cooling a saturated solution in 2-propanol to 5 °C. We did not notice a significant difference in crystal habit or diffraction quality between the two batches.

Uranium(IV) *tert*-butoxide, in our hands, was obtained as green $K[U_2(O\text{-}t\text{-}Bu)_9]\cdot C_6H_{14}$, when following Gilman's procedures.[4,7] It has been noted before[8] that the preparation is not always reproducible and that U(V) alkoxides may be obtained instead of the expected U(IV) compounds. We attribute these difficulties to the relative instability of the U(IV) compound in solution. Only after we established dry and anaerobic conditions very carefully and did not allow

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(7) During early attempts, when using commercial UCl_4, a different type of U(IV) oxo alkoxide was obtained: $U_3O(OCMe_3)_{10}$. A structure determination revealed that it is isostructural with $MoO(O\text{–}neopentyl)_{10}$ (Chisholm, M. H.; Errington, R. J.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 2025) except for the M–M distances, which with U···U = 3.576 (1) Å are outside the range for metal–metal bonding. See: Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Inorg. Chim. Acta* **1984**, *95*, 207.

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0020-1669/84/1323-4211$01.50/0

Table I. Crystallographic Parameters

formula	$KU_2(O\text{-}t\text{-}Bu)_9 \cdot C_6H_{14}$	$U_2(O\text{-}t\text{-}Bu)_9$	$U_2(O\text{-}i\text{-}Pr)_{10}$
fw	1259.38	1134.10	1066.95
space group	$P2_1/c$ (No. 14)	*Pbcm* (No. 57)	$P\bar{1}$ (No. 2)
syst abs	$h0l, l = 2n; 0k0, k = 2n$	$0kl, k = 2n; h0l, l = 2n$	
a, Å	10.713 (3)	13.749 (7)	10.974 (3)
b, Å	25.990 (8)	19.977 (7)	12.226 (3)
c, Å	19.480 (6)	16.923 (8)	10.002 (2)
α, deg	90.0	90.0	111.56 (2)
β, deg	91.13 (5)	90.0	110.09 (2)
γ, deg	90.0	90.0	67.87 (2)
V, Å^3	5423 (2)	4648 (3)	1122.9 (4)
Z	4	4	1
d_{calcd}, g/cm^3	1.542	1.621	1.578
cryst size, mm	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.2	0.3 × 0.2 × 0.2
λ(Mo Kα), cm^{-1}	57.729	66.391	68.67
data collcn instrum	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4	Syntex $P\bar{1}$
Radiation (monochromated in incident beam)	Mo Kα	Mo Kα	Mo Kα
orientation reflcns: no.; range (2θ), deg	25; $9 < 2\theta < 15$	25; $6 < 2\theta < 16$	15; $10 < 2\theta < 18$
temp, °C	23 ± 2	−105 ± 5	23 ± 2
scan method	θ–2θ	θ–2θ	θ–2θ
data collcn range (2θ), deg	$0 < 2\theta < 45$	$0 < 2\theta < 45$	$5 < 2\theta < 50$
no. of unique data; total with $F_o^2 > 3\sigma(F_o^2)$	5382; 2527	3158; 2307	3379; 2719
no. of parameters refined	252	222	115
transmissn factors (max, min)	0.561, 0.315	0.265, 0.136	0.253, 0.127
R^a	0.065	0.044	0.048
$R_w{}^b$	0.083	0.056	0.059
quality-of-fit indicator^c	1.582	1.359	1.148
largest shift/esd, final cycle	<0.5	<0.5	<0.5
largest peak, e/Å^3	<1.0	<1.0	<1.0

^{a} $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^{b} $R_w = \Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c} Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{observns} - N_{parameters})]^{1/2}$.

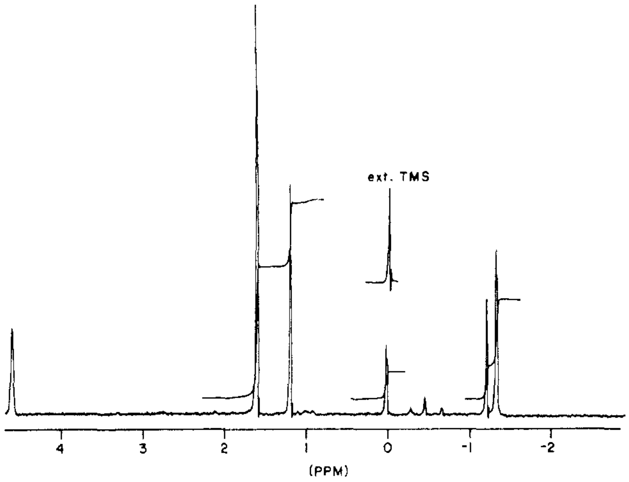

Figure 1. ^1H NMR spectrum of $KU_2(OCMe_3)_9$ in C_6D_6.

the solution to warm up above −10 °C at any time were we able to isolate the U(IV) compound in reasonable yield and pure form. The green compound was recrystallized from hexane solution. The ^1H NMR spectrum (Figure 1) is consistent with the solid-state structure. The green U(IV) *tert*-butoxide **1** slowly transforms into a dark brown [U(V),U(IV)] alkoxide, $U_2(O\text{-}t\text{-}Bu)_9$ (**2**), in hexane solution. Dichroic crystals (black and light brown) of excellent quality were obtained at 5 °C over a period of 3 weeks.

Spectroscopic Measurements. ^1H NMR spectra were measured on a Varian EM-390 spectrometer at room temperature. UV/vis spectra were recorded on a Cary-17D spectrometer.

X-ray Procedures. The crystallographic work was mostly routine and followed procedures that have previously been described.[9] Many of the relevant data are summarized in Table I, and an extended account of the handling of each structure is available in the supplementary material. The atomic positions for compounds **1**–**3** are listed in Tables II–IV, respectively.

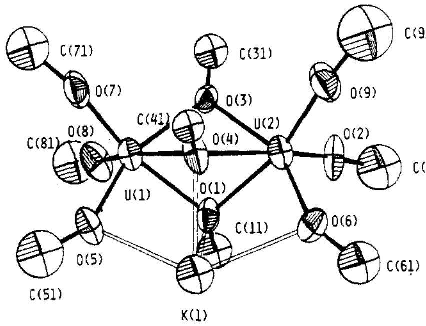

Figure 2. View of central portion of the $KU_2(OCMe_3)_9$ molecule showing the atomic numbering scheme.

Structural Results

Selected bond distances and angles are listed in Table V for all three compounds. Complete lists are available as supplementary material.

$KU_2(OCMe_3)_9 \cdot C_6H_{14}$ (1). Crystals of this compound consist of a regular array of $K^+[U_2(OCMe_3)_9^-]$ ion pairs with partly disordered hexane molecules as solvent of crystallization. The configuration of the dinuclear species is that of a face-sharing octahedron (Figure 2). The $[U_2(OCMe_3)_9]^-$ anion and the K^+ ion form a tight ion pair, with the K^+ ion cradled by two bridging and two terminal oxygen atoms at distances of 2.75 [2] and 2.93 [2] Å. There are no intermolecular bonding interactions, and it is thus not surprising that this compound, even though formally ionic, dissolves readily in nonpolar solvents such as hexane. The U···U distance is 3.631 (1) Å. Averaged U–O bond lengths are 2.13 [1] and 2.42 [3] Å for the terminal and the briding oxygen atoms, respectively. The $U\text{–}O_t\text{–}C$ bond angles are 168–175° for the alkoxides not involved in K^+ bonding and 152 [1]° for the latter.

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[9] (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. (c) North, A. C. T.; Phillips, D. C.; Mathews, F. A. *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr. Theor. Gen. Crystallogr.* **1968**, *A24*, 351. (d) Calculations were done on a VAX 11/780 computer with software from the Enraf-Nonius VAX-SDP package. (e) Data for $KU_2(OCMe_3)_9$ and $U_2(OCMe_3)_9$ were collected by Molecular Structure Corp., College Station, TX.

Table II. Final Positional Parameters for $KU_2(OCMe_3)_9$

atom	x	y	z	B,[a] Å^2
U(1)	0.3465 (1)	0.35839 (5)	0.31362 (7)	3.73 (3)
U(2)	0.2467 (2)	0.48466 (5)	0.25469 (7)	3.84 (3)
O(1)	0.163 (2)	0.4125 (7)	0.319 (1)	4.1 (6)
O(2)	0.199 (2)	0.5454 (8)	0.322 (1)	5.4 (6)
O(3)	0.414 (2)	0.4443 (8)	0.320 (1)	3.8 (6)
O(4)	0.300 (2)	0.4016 (7)	0.205 (1)	4.2 (6)
O(5)	0.223 (2)	0.2984 (8)	0.280 (1)	5.4 (7)
O(6)	0.077 (2)	0.4808 (9)	0.195 (1)	5.3 (6)
O(7)	0.516 (2)	0.3252 (8)	0.284 (1)	5.7 (7)
O(8)	0.360 (2)	0.3370 (9)	0.419 (1)	6.1 (7)
C(61)	−0.025 (4)	0.504 (2)	0.157 (2)	7 (1)*
O(9)	0.360 (2)	0.5303 (8)	0.189 (1)	5.8 (7)
K(1)	0.0549 (9)	0.3685 (3)	0.2053 (5)	6.1 (2)*
C(12)	0.028 (3)	0.361 (1)	0.395 (2)	5.6 (9)*
C(11)	0.078 (4)	0.416 (1)	0.377 (2)	6 (1)*
C(21)	0.145 (5)	0.593 (2)	0.359 (3)	10 (2)*
C(31)	0.517 (4)	0.467 (1)	0.347 (2)	6 (1)*
C(32)	0.616 (5)	0.472 (2)	0.299 (3)	10 (2)*
C(41)	0.354 (3)	0.393 (1)	0.140 (2)	4.2 (8)*
C(42)	0.277 (4)	0.425 (2)	0.082 (2)	8 (1)*
C(43)	0.344 (4)	0.333 (1)	0.121 (2)	6 (1)*
C(72)	0.735 (4)	0.331 (2)	0.254 (2)	9 (1)*
C(71)	0.631 (4)	0.293 (2)	0.275 (2)	8 (1)*
C(51)	0.196 (5)	0.248 (2)	0.271 (3)	10 (1)*
C(81)	0.379 (5)	0.322 (2)	0.488 (3)	10 (1)*
C(13)	0.150 (4)	0.442 (1)	0.441 (2)	6 (1)*
C(34)	0.589 (5)	0.433 (2)	0.399 (3)	10 (2)*
C(14)	−0.038 (4)	0.447 (1)	0.351 (2)	6 (1)*
C(33)	0.497 (5)	0.520 (2)	0.379 (3)	11 (2)*
C(62)	−0.099 (5)	0.544 (2)	0.196 (3)	11 (2)*
C(82)	0.267 (5)	0.290 (2)	0.506 (3)	12 (2)*
C(83)	0.376 (6)	0.359 (2)	0.545 (3)	13 (2)*
C(23)	0.228 (7)	0.593 (3)	0.423 (4)	18 (3)*
C(22)	0.170 (6)	0.636 (2)	0.308 (3)	13 (2)*
C(63)	0.026 (6)	0.533 (2)	0.094 (3)	13 (2)*
C(64)	−0.110 (5)	0.464 (2)	0.132 (3)	12 (2)*
C(44)	0.488 (4)	0.408 (2)	0.140 (2)	7 (1)*
C(73)	0.604 (5)	0.264 (2)	0.203 (3)	12 (2)*
C(52)	0.247 (5)	0.218 (2)	0.332 (3)	12 (2)*
C(3)	−0.026 (7)	0.325 (3)	−0.009 (3)	16 (2)*
C(4)	−0.215 (7)	0.326 (3)	0.037 (4)	18 (3)*
C(5)	−0.092 (6)	0.305 (2)	0.046 (3)	14 (2)*
C(7)	−0.108 (6)	0.249 (2)	0.025 (3)	15 (2)*
C(6)	−0.057 (5)	0.313 (2)	0.104 (3)	10 (1)*
C(54)	0.203 (6)	0.229 (3)	0.201 (3)	16 (2)*
C(53)	0.061 (6)	0.242 (3)	0.291 (3)	15 (2)*
C(74)	0.661 (6)	0.270 (2)	0.343 (3)	14 (2)*
C(84)	0.472 (7)	0.282 (3)	0.485 (4)	18 (3)*
C(91)	0.430 (6)	0.569 (2)	0.148 (3)	13 (2)*

[a] In this and the following tables, starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

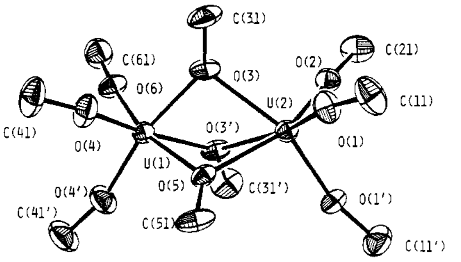

Figure 3. View of the central portion of the $U_2(OCMe_3)_9$ molecule showing the atomic numbering scheme.

$U_2(OCMe_3)_9$ (2). Crystals of this compound contain discrete molecules, shown in Figure 3. The configuration is similar to that in **1**, viz. face-sharing bioctahedral. The U···U distance is 3.549 (1) Å. The U–O bond lengths are distinctly different for the two uranium atoms. U(1) has U–O distances of 2.069 [6] and 2.258 [11] Å for the terminal and bridging oxygen atoms, respectively. The corresponding bond lengths for U(2) are 2.106 [1] and 2.49 [2] Å. The U–O–C bond angles in the terminal alkoxides range from 164 to 176°.

$U_2(OCHMe_2)_{10}$ (3). Discrete molecules of **3** reside on inversion centers. The molecular structure is shown in Figure 4. It is edge-sharing bioctahedral with a U···U distance of

Table III. Final Positional Parameters for $U_2(OCMe_3)_9$

atom	x	y	z	B, Å^2
U(1)	0.14919 (4)	0.89661 (3)	0.750	2.41 (1)
U(2)	0.32808 (5)	1.02469 (3)	0.750	2.47 (1)
O(1)	0.3368 (6)	0.4050 (4)	0.3424 (5)	3.6 (2)
O(2)	0.5259 (8)	0.4927 (6)	0.750	3.1 (3)
O(3)	0.2715 (6)	0.5728 (4)	0.3307 (4)	3.0 (2)
O(4)	0.0477 (6)	0.6145 (4)	0.3396 (6)	4.2 (2)
O(5)	0.1506 (8)	0.4897 (5)	0.250	2.5 (2)
O(6)	0.1907 (9)	0.7026 (5)	0.250	3.3 (3)
C(11)	0.362 (1)	0.3483 (7)	0.391 (1)	5.1 (4)
C(12)	0.530 (1)	0.665 (1)	0.618 (1)	8.3 (5)
C(13)	0.352 (2)	0.3685 (9)	0.478 (1)	10.1 (6)
C(14)	0.302 (2)	0.2912 (9)	0.372 (2)	18.3 (8)
C(21)	0.427 (1)	0.476 (1)	0.750	4.3 (5)
C(22)	0.380 (1)	0.5031 (8)	0.675 (1)	6.1 (4)
C(23)	0.422 (2)	0.398 (1)	0.750	6.7 (7)
C(31)	0.291 (1)	0.5775 (7)	0.4160 (8)	4.5 (3)
C(32)	0.219 (1)	0.5288 (7)	0.4580 (8)	5.0 (4)
C(33)	0.395 (1)	0.5579 (9)	0.4315 (8)	5.9 (4)
C(34)	0.270 (1)	0.6520 (7)	0.4406 (9)	6.1 (4)
C(41)	0.030 (1)	0.3613 (7)	0.610 (1)	5.4 (4)
C(42)	0.041 (2)	0.2881 (8)	0.624 (1)	9.7 (6)
C(43)	0.991 (2)	0.623 (1)	0.473 (1)	11.6 (6)
C(44)	0.126 (2)	0.396 (1)	0.636 (2)	12.5 (8)
C(51)	0.069 (1)	0.4393 (9)	0.250	3.8 (4)
C(52)	0.112 (2)	0.373 (1)	0.250	15 (2)
C(53)	−0.016 (2)	0.551 (1)	0.688 (2)	28.0 (8)
C(61)	0.232 (1)	0.731 (1)	0.750	4.8 (5)
C(62)	0.341 (2)	0.760 (1)	0.250	7.8 (7)*
C(63)	0.202 (1)	0.6955 (9)	0.675 (1)	6.9 (4)*

Table IV. Final Positional Parameters for $U_2(OCHMe_2)_{10}$

atom	x	y	z	B, Å^2
U(1)	0.38033 (7)	0.15761 (6)	0.06092 (8)	6.01 (2)
O(11)	0.462 (1)	−0.0402 (9)	0.077 (1)	6.5 (3)
C(11)	0.410 (3)	−0.080 (3)	0.172 (4)	16 (1)*
C(12)	0.312 (4)	−0.140 (3)	0.090 (4)	20 (1)*
C(13)	0.507 (4)	−0.085 (4)	0.302 (5)	22 (2)*
O(21)	0.231 (1)	0.108 (1)	−0.118 (2)	9.6 (5)
C(21)	0.110 (4)	0.117 (3)	−0.222 (4)	18 (1)*
C(22)	0.100 (4)	0.168 (3)	−0.336 (4)	19 (1)*
C(23)	0.011 (4)	0.081 (4)	−0.189 (5)	21 (2)*
O(31)	0.533 (1)	0.200 (1)	0.234 (1)	9.6 (5)
C(31)	0.619 (4)	0.261 (3)	0.349 (4)	19 (1)*
C(32)	0.616 (4)	0.239 (4)	0.484 (5)	21 (2)*
C(33)	0.690 (4)	0.325 (3)	0.336 (4)	20 (1)*
O(41)	0.335 (1)	0.316 (1)	0.008 (2)	10.7 (5)
C(41)	0.291 (4)	0.441 (3)	0.009 (4)	19 (1)*
C(42)	0.290 (5)	0.459 (4)	−0.133 (5)	23 (2)*
C(43)	0.260 (6)	0.522 (5)	0.121 (6)	28 (2)*
O(51)	0.253 (1)	0.223 (1)	0.197 (1)	10.2 (5)
C(53)	0.200 (6)	0.373 (5)	0.398 (6)	29 (2)*
C(52)	0.085 (6)	0.237 (5)	0.297 (6)	28 (2)*
C(51)	0.149 (4)	0.298 (4)	0.279 (5)	21 (2)*

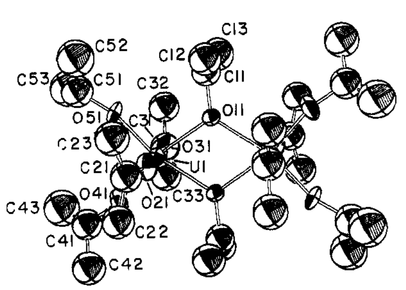

Figure 4. View of the $U_2(OCHMe_2)_{10}$ molecule showing the atomic numbering scheme.

Table V. Selected Bond Distances (Å) and Angles (deg)

A. For $KU_2(O\text{-}t\text{-}Bu)_9$

Bond Distances

U(1)-U(2)	3.631 (2)	U(2)-O(4)	2.44 (2)
U(1)-O(1)	2.42 (2)	-O(2)	2.12 (2)
-O(3)	2.35 (2)	-O(6)	2.14 (2)
-O(4)	2.44 (2)	-O(9)	2.14 (2)
-O(5)	2.14 (2)	K(1)-O(1)	2.74 (2)
-O(7)	2.10 (2)	-O(4)	2.76 (2)
-O(8)	2.13 (2)	-O(5)	2.93 (2)
U(2)-O(1)	2.44 (2)	-O(6)	2.94 (2)
-O(3)	2.42 (2)		

Bond Angles

U(1)-O(1)-U(2)	96.6 (6)	U(2)-O(1)-C(11)	126 (2)
-O(3)-U(2)	99.1 (7)	-O(2)-C(21)	168 (2)
-O(4)-U(2)	96.0 (6)	-O(3)-C(31)	127 (2)
-O(1)-C(11)	126 (2)	-O(4)-C(41)	127 (2)
-O(3)-C(31)	133 (2)	-O(6)-C(61)	153 (2)
-O(4)-C(41)	128 (2)	-O(9)-C(91)	171 (2)
-O(5)-C(51)	151 (2)	O(1)-U(1)-O(3)	72.3 (6)
-O(7)-C(71)	168 (2)	-O(4)	67.7 (6)
-O(8)-C(81)	175 (2)	-U(2)-O(3)	70.8 (6)
		-O(4)	67.5 (6)
O(2)-U(2)-O(1)	99.0 (6)	O(6)-U(2)-O(1)	85.8 (7)
-O(3)	100.3 (7)	-O(2)	99.2 (8)
-O(4)	165.0 (6)	-O(3)	151.5 (7)
-O(9)	96.0 (7)	-O(4)	86.8 (7)
O(3)-U(1)-O(4)	70.7 (6)	-O(9)	100.8 (8)
-U(2)-O(4)	69.6 (6)	O(7)-U(1)-O(1)	163.4 (6)
O(5)-U(1)-O(1)	86.5 (7)	-O(3)	97.9 (7)
-O(3)	153.8 (7)	-O(4)	96.7 (7)
-O(4)	87.4 (7)	O(8)-U(1)-O(1)	98.4 (7)
-O(7)	98.7 (7)	-O(3)	100.4 (7)
-O(8)	97.8 (7)	-O(4)	165.0 (7)
		-O(7)	96.5 (8)
		O(9)-U(2)-O(1)	162.4 (6)
		-O(3)	97.6 (7)
		-O(4)	96.4 (6)

B. For $U_2(O\text{-}i\text{-}Pr)_{10}$

Bond Distances

U(1)-U(1)	3.789 (1)	U(1)-O(31)	2.02 (1)
U(1)-O(11)	2.29 (1)	-O(41)	2.03 (1)
U(1)-O(11)′	2.28 (1)	-O(51)	2.03 (1)
-O(21)	2.05 (1)		

Bond Angles

U(1)-O(11)-U(1)	111.4 (5)	U(1)-O(41)-C(41)	164 (3)
-C(11)	128 (2)	-O(51)-C(51)	165 (3)
-O(21)-C(21)	160 (2)	O(11)-U(1)-O(11)	68.6 (5)
-O(31)-C(31)	163 (2)		

C. For $U_2(O\text{-}t\text{-}Bu)_9$

Bond Distances

U(1)-U(2)	3.549 (1)	U(2)-O(1)	2.106 (7)
U(1)-O(3)	2.251 (7)	-O(2)	2.107 (10)
-O(4)	2.073 (7)	-O(3)	2.502 (7)
-O(5)	2.271 (9)	-O(5)	2.457 (9)
-O(6)	2.062 (10)		

Bond Angles

U(1)-O(3)-U(2)	96.5 (2)	O(2)-U(2)-O(3)	93.4 (3)
-O(5)-U(2)	97.2 (3)	-O(5)	155.6 (3)
-O(4)-C(41)	164.2 (8)	O(3)-U(1)-O(3′)	74.7 (3)
-O(6)-C(61)	173 (1)	-O(5)	73.9 (3)
-O(5)-C(51)	131.6 (9)	-U(2)-O(3)	66.1 (3)
-O(3)-C(31)	135.5 (7)	-O(5)	66.4 (2)
U(2)-O(2)-C(21)	176 (1)	O(4)-U(1)-O(4)	94.0 (5)
-O(1)-C(11)	163.9 (8)	-O(3)	95.1 (3)
-O(3)-C(31)	121.9 (7)	-O(5)	96.5 (3)
-O(5)-C(51)	131.2 (9)	-O(6)	94.8 (3)
O(1)-U(2)-O(1)	95.9 (4)	O(6)-U(1)-O(3)	93.1 (3)
-O(3)	97.6 (3)	-O(5)	163.4 (4)
-O(5)	97.7 (2)		
-O(2)	98.5 (3)		

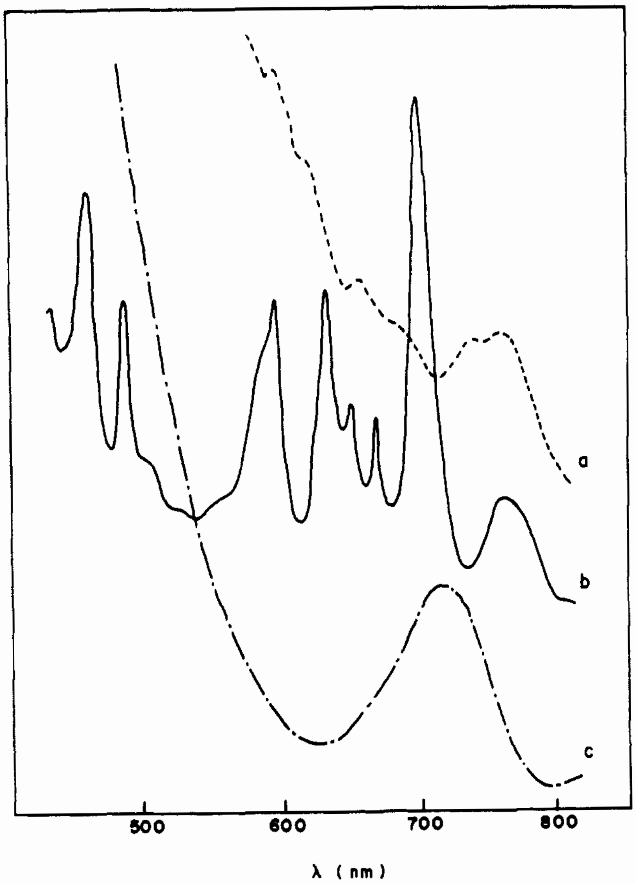

Figure 5. Visible spectra of (a) $U_2(OCMe_3)_9$, (b) $KU_2(OCMe_3)_9$, and (c) $U_2(OCHMe_2)_{10}$ all in hexane.

3.789 (1) Å. The U–O distances are 2.03 [1] and 2.29 [1] Å for the terminal and bridging oxygen atoms, respectively. The U–O_t–C bond angles cover a range between 160 and 165°.

Comparison of the Structures. Starting with the [U(V),U(V)] dimer, **3**, we find a U···U distance that is clearly outside the range of metal–metal bonding and indicates, instead, a repulsive metal–metal interaction. The bond angles around the bridging oxygen atoms (O_{br}) as well as around the uranium center are distorted so as to release strain from a repulsive potential between the metal atoms, which is always underlying, regardless of the electron configuration. In the idealized case of an edge-sharing bioctahedron the M–O_{br}–M angle and the O_{br}–M–O_{br} angles are 90°, whereas we find an opening of the M–O_{br}–M angle to 111.4 (5)° along with an acute O–M–O angle, 68.6 (5)°.

The geometrical properties of face-sharing bioctahedral structures, as found in compounds **1** and **2**, have been treated in detail before.[10] The values for the idealized M–O_{br}–M and O_{br}–M–O_{br} are 70.53 and 90°, respectively. We find them distorted in both **1** and **2** in a way that responds to repulsive strain between the metal centers. That we are dealing with noninteracting metal centers is especially apparent from the metric and spectral behavior of the mixed-valence species **2**. The U–O bond lengths for U(1) correspond, within the standard deviations, to those observed in the (U^V, U^V) dimer, **3**, whereas U(2) shows U–O bond lengths that appear to be typical for U^{IV}, as in compound **1**. Consistent with the structural indication that there are discrete, trapped valence states in **2**, its visible spectrum can be rationalized by superposition of the spectra of **1** and **3** (Figure 5).

A feature common to all three compounds is the unusual bonding of the terminal alkoxides. The U–O_t–C bond angles

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(10) Cotton, F.A.; Ucko, D. A. *Inorg. Chim. Acta* **1971**, *6*, 161.

fall into a range between 160 and 176°, which suggests a hybridization of the oxygen atoms close to sp. Naturally, the bond angles around the oxygen atoms involved in the potassium binding are somewhat smaller, ca. 152°, in order to direct electron pairs toward the K^+ ions.

The only compound on record similar to the three alkoxides is $U_2(C_3H_5)_4(OCMe_3)_4$.[11] A comparison of respective bond lengths reveals that U–O distances are by no means of diagnostic value to determine the oxidation state of the involved uranium center. They can only be so used when the compounds being compared are otherwise very similar, as is the case with **1** and **2**. The U–O_t–C groups in the allyl compound are also linear within the standard deviations.

Discussion

The starting point for this investigation was the question of how closely uranium in its oxidation states IV and V would resemble the group 6 transition elements. We have found that, in spite of structural configurations of the dinuclear unit that are compatible with metal–metal bond formation, 5f–5f overlap is insufficient to stabilize uranium–uranium bonds, at least in these alkoxide compounds. We might then ask whether the chemistry of uranium resembles that of any other group of transition metals. It has been noted before[12] that in some reactions uranium parallels the chemical behavior of the very early transition metals, in particular that of titanium and zirconium. There are, indeed, some analogies. The degree of polymerization of titanium and uranium alkoxides depends critically on the bulkiness of the hydrocarbon residue attached to the oxygen atom.[13,14] Perhaps an even more striking analogy is found in the bonding mode of the terminal alkoxide residues, where for both titanium and uranium the M–O–C bond angles are close to linearity. However, this effect is most pronounced in the uranium compounds, since the most obtuse Ti–O–C bond angle on record is only 166.2°.[15]

The linearization of M–O–C bonds is generally attributed to the formation of O $\pi \rightarrow$ M dative bonds from both, rather than only one, of the oxygen lone-pair orbitals.[16] We believe that explanation is applicable here. The unprecedented extent of such O $\pi \rightarrow$ M bonding when M is a uranium atom raises interesting theoretical problems that have yet to be addressed. Apparently the s–f orbitals of uranium are better acceptor orbitals than the 4d or 5d orbitals of molybdenum or tungsten. To some extent, the formation of O $\pi \rightarrow$ U bonds may be competitive with the formation of U–U bonds. If that is an important factor, then we can now recognize, by hindsight, that in a quest for U–U bonds alkoxide compounds may not constitute the most propitious class to examine. That this may indeed be the case is suggested by our recent observation[16] that substitution of a chloride ligand by an alkoxide ligand led to the lengthening of a metal–metal bond. An alkoxide ligand as a donor of three or more electrons is comparable to ligands such as dialkylamides (NR_2^-) and it is known that $Mo(NMe_2)_4$ is monomeric.[1] It is interesting to see that in case of the previously cited $U_2(C_3H_5)_4(OCMe_3)_4$ the bond angle U–O_t–C is linear within the esd. It appears that in this case the highest possible degree of π overlap with the single terminal alkoxide is achieved as the remaining two allyl ligands provide only a total of eight electrons while occupying four coordination sites.

In conclusion, an optimum strategy toward forming metal–metal bonds between uranium(IV) atoms would now appear to involve dinuclear, bridged species with terminal ligands incapable of π donation. Mimicking the chemistry of metal–metal-bonded compounds of the early transition metals, using ligands other than alkoxides would seem to be most promising.

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Supplementary Material Available: Detailed crystallographic discussion and tables of structure factors, thermal parameters, bond angles, and nonbonded contacts less than 4.0 Å (75 pages). Ordering information is given on any current masthead page.

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